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Meeting the needs for released nanomaterials required for further testing – the SUN approach

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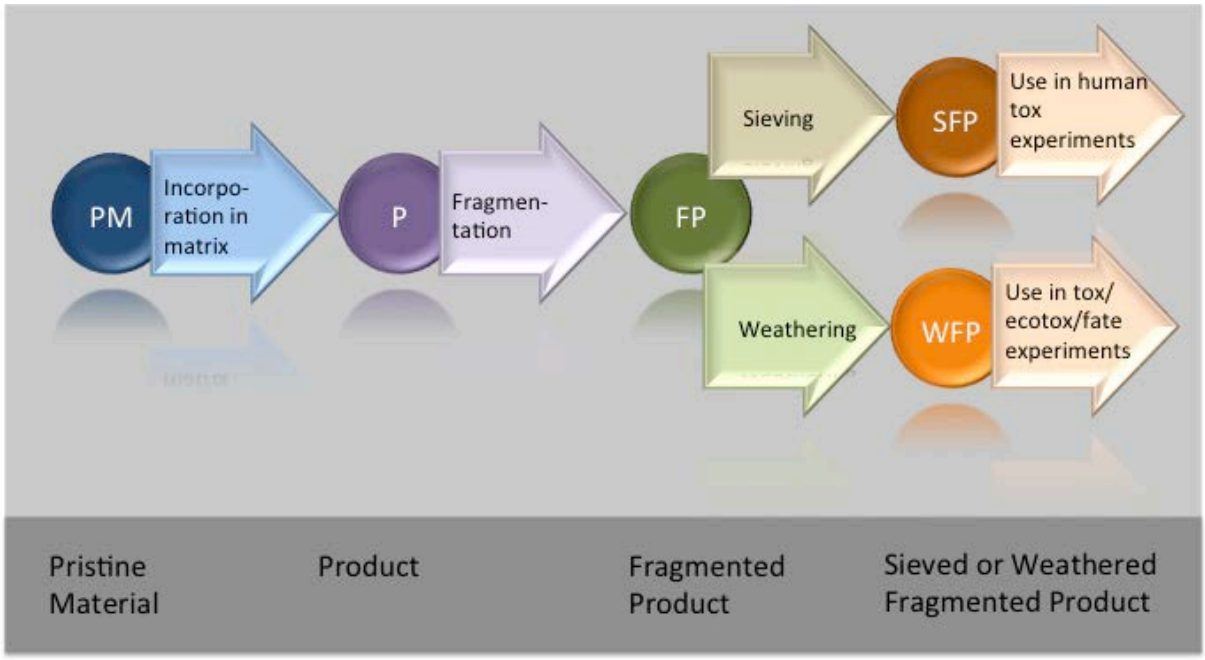

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Abstract

The analysis of the potential risks of engineered nanomaterials (ENM) has so far been almost exclusively focused on the pristine, as-produced particles. However, when considering a life-cycle perspective, it is clear that ENM released from genuine products during manufacturing, use, and disposal is far more relevant. Research on release of materials from nano-products is growing and the next necessary step is to investigate the behavior and effects of these released materials in the environment and on humans. Therefore, sufficient amounts of released materials need to be available for further testing. In addition, ENM-free reference materials are needed since many processes not only release ENM but also nano-sized fragments from the ENM-containing matrix that may interfere with further tests. The SUN consortium (Project on "Sustainable Nanotechnologies", EU 7th Framework funding) uses methods to characterize and quantify nanomaterials released from composite samples that are exposed to environmental stressors. Here we describe an approach to provide materials in hundreds of gram quantities mimicking actual released materials from coatings and polymer nanocomposites by producing what is called "Fragmented Products" (FP). These FP can further be exposed to environmental conditions (e.g. humidity, light) to produce "Weathered Fragmented Products" (WFP) or can be subjected to a further size fractionation to isolate "Sieved Fragmented Products" (SFP) that are representative for inhalation studies. In this perspective we describe the approach, and the used methods to obtain released materials in amounts large enough to be suitable for further fate and (eco)toxicity testing. We present a case study (nanoparticulate organic pigment in polypropylene) to show exemplarily the procedures used to produce the FP. We present some characterization data of the FP and discuss critically the further potential and the usefulness of the approach we developed.

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Introduction

An increasing number of products incorporating engineered nanomaterials (ENM) has reached the market[1, 2]. In these products, ENM are incorporated in different solid or liquid matrices as for example CNT in plastics[3], nano-TiO_2 in ceramics[4], cement[5], cosmetics[6] and paints[7] or nano-SiO_2 in food[8]. ENM may be released from ENM-containing products during the use or end-of-life phase. Gathering information on the release of ENM from products at different stages of their value chain is therefore important for defining the hot spots of release and for assessing the human and environmental exposure needed for a realistic risk assessment[9-12].

The properties of the materials emitted from the nano-products during the manufacturing, use or end-of-life phase are dominated by the matrix and the incorporation of the ENM into the matrix (i.e. surface-bound or internally embedded)[13, 14]. The materials released from paints for example consist mainly of paint fragments with incorporated nanoparticles[15-17]. Comparable observations were made for CNT-epoxy and CNT-polyurethane composites: fragmentation or weathering resulted mainly in the release of composite fragments with bound CNTs[18, 19]. The methodology of aging-sampling-characterization of released materials has undergone first interlaboratory comparisons with reproducible observations on silica ENM in plastics[20].

Transformation reactions may affect the composition of the released materials. Whereas the pristine materials may be released during production and manufacturing, the materials liberated during use and disposal may be transformed to some extent. It has been shown that sunscreen TiO_2 composite nanomaterials are significantly altered by exposure to water and sunlight[21-23], changing their physico-chemical behavior. Consequently, the effects of altered TiO_2 on organisms differ from the one of pristine nano-TiO_2 as well as from TiO_2 composites[24-26]. Al-Kattan et al.[27] have shown that TiO_2 released from paint has different colloidal behavior than the pristine TiO_2 before incorporation into the paint, being much more stable in the presence of Ca.

These studies show how important it is to evaluate the complete life-cycle of materials containing ENM, as during the different stages materials may be imposed to very diverse chemical and physical conditions that can strongly affect their properties[28].

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Whereas the definition of the pristine ENM is straightforward - the as-produced materials in pure form - it is less clear what we mean by “aged”, “transformed”, “weathered” or “released” ENM. A classification can be centered on the ENM itself and possible changes during different life-cycle stages[29]. After ENM are released from products and are changed by environmental processes, they can be classified as environmentally transformed ENM. “Weathered” and “aged” ENM are synonyms for ENM that were exposed to environmental conditions with “transformed” ENM being the result of these reactions. These three designations can be used interchangeably. Aging, transformation and weathering can be carried out using pure pristine materials that are exposed to environmental stressors. Examples include the transformation of TiO_2-nanomaterials used in sunscreens by UV light[21] or the sulfidation of nano-Ag[30].

As we have stated above, most ENM in products are incorporated into a matrix or present on the surface of a matrix. Thus, these ENM are not available as pure material. ENM released by different mechanisms can be present in free form or bound to the matrix[13]. Under environmental conditions these materials represent the most realistic form of the ENM that enters the environment or that consumers are exposed to. Knowledge on released materials is bound to knowledge on the use of the nano-enabled products during their life-cycle (or different life-cycles)[28].

In the following we use “released materials” when all the particles released from a matrix are referred to, and use “released ENM” when we only refer to the ENM that are released, either in free or embedded form.

Current state on production of aged and released materials

While the need to use released materials in environmental and human fate and exposure studies is clear, it is less straightforward how to obtain and handle released materials. The released materials are not only containing ENM but also matrix fragments, often also in the nano-range. Any (eco)toxicological experiment with released materials should therefore always include the matrix without the ENM in order to relate any effect to the nanomaterial and not to be confounded by possible matrix toxicity. This means that such experiments can only be carried out with matrices specifically produced for experiments, as the nano-free control sample needs to be prepared with the same matrix. Commercially available products

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intended for testing face the problem that exactly the same product without ENM (pure matrix) would be needed, which is not possible in most cases. There might also be synergistic effects of matrix and ENM, generating released materials different chemistry to the pristine ENM. If the matrix that is used in actual products cannot be tested alone, then a comparative understanding of the effects of matrix and ENM may not be achievable.

Having a matrix with ENM available then brings us to the next point: How to produce and collect sufficiently high amounts of released materials? Ecotoxicological experiments often require gram to even kilogram quantities of materials, e.g., in sediment or soil exposure or mesocosm studies. When the ENM is contained in a solid matrix or in a surface coating, collecting released materials becomes challenging. For example, a leachate from a weathering experiment of a surface coating may only contain ENM in the µg/l level and the highest observed concentrations of Ag and TiO_2 in washing liquids from nano-textiles were in the range of mg/l[31, 32], meaning that any extraction and collection of these materials for further experiments is not feasible. Standard tests that are used in many aging studies such as the Taber abrasion test were developed to investigate the remaining material, not the released fraction[33]. Although procedures have been developed to collect materials released in such tests and also perform toxicological tests on them[34], the amounts that can be collected with reasonable effort are smaller than required by the SUN project partners. Based on these facts, it is unrealistic to obtain a sufficiently high amount of the released ENM fraction under conditions that are fully representative for real-world conditions.

Alternative approaches have to be applied to produce sufficient amounts for risk assessment studies of “released” ENM. Released fragments of polymer nanocomposites were already produced by abrasion in amounts sufficient for in vitro studies[19, 34]. In the NanoHouse project, fragments of a paint were produced by milling and these fragments were exposed to UV light to further age them[35]. The milling was intended to increase the available surface area of the material for release and weathering. The particle size distribution of the milled paint was in the µm range with a peak at 10 µm[15]. These paint fragments represent to some extent released paint fragments observed in field studies[36, 37]. When the milled and aged paint is extracted with water, a stable suspension with up to 500 µg/l Ti could be obtained using 20 g/l of paint powder[27]. The aged paint powder was then used in toxicological studies, both *in vitro*[38] and *in vivo*[39]. Another approach has also been published where paint was

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applied on boards and sanding dust was collected and then used in *in vitro* tests[40] as released fraction.

The SUN approach

The SUN project on "Sustainable Nanotechnologies" aims to evaluate environmental, health and safety risks during the entire life cycle of manufactured nanomaterials and to incorporate the results into tools and guidelines for more sustainable manufacturing. To achieve this goal, the focus of the project is not only on the pristine ENM but more on actual nanoproducts in the form of case studies. It is therefore necessary to collect and characterize ENM released from the materials used in the SUN case studies in different life cycle stages for use in nano(eco)toxicological and behavior/fate studies. The formulated materials are coatings, composites or powder mixtures and represent the actual forms in which ENM are used in the real world. The key requirements identified by SUN partners for producing released ENM are:

- To use formulated materials instead of just aging pristine particles;
- The process is reliable and quick;
- The samples are close to real-world exposure, such that assays can be prepared for "released" materials;
- They have to be available in a sufficient amount (hundreds of grams to kg) for testing in nano(eco)toxicity studies and with relevant size distribution;
- A nano-free formulated material is available as reference.

Using these criteria, the SUN partners used a consensus process to devise a method to produce materials representing released and aged ENM considering the results from the published release studies discussed above. Depending on the incorporation of the ENM into the matrix and the properties of the matrix, different methods are necessary to produce "fragmented products" (FP). The obtained FP represent a form of the matrix with a greatly increased surface area, but constitute otherwise the identical material to the one in the real products. Within SUN, the elasticity modulus of the matrix, a mechanical material property, which can be identified by oscillatory stress-strain dynamical mechanical analysis, is proposed as criterion for FP processing. For matrices with an elasticity modulus in the range of 10^9 Pa, fragmentation of the matrix with or without ENM can successfully be performed

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186 by cryomilling to simulate the materials' life cycle. Due to the freezing the material gets very
187 brittle and therefore cryomilling can be regarded as a worse case scenario during the life
188 cycle of the material. In addition, cryomilling applies a much higher wear energy compared
189 to sanding which is known as a high mechanical stress inducing operation and therefore
190 releases more airborne particles compared to other handling or processing operations[41]. For
191 materials whose behavior under tensile load is comparable to a gel the such as in the case of
192 the CuO containing antimicrobial coating, cryomilling has proven to be not suitable to obtain
193 FP due to their viscoelastic behavior, which leads to a re-flow of the material. In the specific
194 case, this is attributed to the acrylic, non-crosslinked matrix. Therefore, viscoelastic
195 materials need another approach for FP production, which is realized within SUN by coating
196 the material onto a hard substrate. In this case the mechanical properties are dominated by
197 the hard support. FP production can be performed either by cryomilling of scraped-off flakes
198 or sanding of the dried, supported coating. In the latter case, the sanding dust could be
199 collected as FP and would represent a realistic life cycle released material consisting of
200 coating fragments, which coexist with or are attached to substrate fragments.
201 Within SUN eight case studies are carried out, representing important uses of ENM in
202 products. Table 1 shows the different procedures to obtain FP for these case studies as well
203 as resulting FP sizes. The diameter d_{10} represents the smallest 10% of the particles in volume
204 metrics.

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205 ***Table 1: Overview of chosen fragmentation methods for each SUN case study, and of resulting fragment products (FP) and "Sieved Fragmented***

206 ***Products" (SFP) sizes and amounts.***

Case study	**ENM @ matrix**	**Fragmentation method** **The sizes indicated are in volume metrics**	**Elasticity modulus of matrix (Pa)**	**Size of FP**	**FP produced**	**SFP pro**
CNT in antifouling coating	a) CNT @ epoxy	a) Cryomilling of compounded plates	a) $2.8*10^9$	d_{10}: 96 µm, d_{50}: 164 µm and d_{90}: 263 µm	180 g	3.1
	b) CNT @ silicone epoxy	b) Painting of compounded paint onto a hard substrate and cryomilling of scraped-off flakes	b) 10^8 (low viscous flow)	d_{10}: 77 µm, d_{50}: 182 µm and d_{90}: 386 µm	900 g	-
Inorganic pigment in polymer	Fe_2O_3 @ PE	Cryomilling of compounded granulates	$1.7*10^9$	d_{10}: 101 µm, d_{50}: 154 µm and d_{90}: 314 µm	900 g	-
Organic pigment in polymer	DPP @ PP	Cryomilling of compounded granulates	$9.7*10^8$	d_{10}: 70 µm, d_{50}: 146 µm and d_{90}: 272 µm	900 g	2.8
CNT in lightweight conductive polymer	CNT @ PP	Cryomilling of compounded granulate	$9.7*10^8$	d_{10}: 69 µm, d_{50}: 131 µm and d_{90}: 229 µm	900 g	5.4
CuO antimicrobial coating	CuO @ acrylic paint on wood	Preparation of paint films on PE foils. Mortar grinding of paint film (removed from PE) in liquid nitrogen. Transfer of FP to an aqueous phase before complete warm up to room temperature to prevent aggregation.	10^{-7} (viscoelastic)	d_{10}: 20 µm, d_{50}: 73 µm and d_{90}: 190 µm	10 g	-
Antifriction coating	WC @ Co on steel	Coating onto a substrate and fragmentation of scraped-off flakes by wet ball milling	-			
Self-cleaning coating for ceramic tiles	TiO_2 @ ceramics	No process foreseen in SUN, due to thinness of TiO_2 coating so that any mechanically generated FP would be completely dominated by ceramic support.	-			
Pancake mixture	SiO_2 @ flour	No fragmentation needed, *in vitro* digestion considered	-			

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The obtained FP can undergo further processing, including size separation and/or weathering. FP is sieved into "Sieved Fragmented Products" (SFP) either for characterization purposes or to obtain FP samples of wanted size distribution for further testing.

In order to obtain samples close to exposure as expected in environmental settings, weathering can be applied to the FP to generate "Weathered Fragmented Products" (WFP). FP used in coatings or composites which are typically exposed to sunlight during the use-phase are weathered in a Suntest apparatus (Atlas, US) according to an ISO guideline[42]. The Suntest apparatus emits simulated solar radiation, which is comparable to natural sunlight with regard to the emitted spectrum as well as to the applied irradiance.

When these WFP are then tested under environmentally relevant conditions in toxicological or ecotoxicological test media, e.g. soil, sediments or water, they undergo further changes resulting in "Aged Fragmented Products" (AFP). This aging reaction depends on the type and composition of the medium and is specific for each test. The weathering is carried out after fragmentation, so on FP and not the formulated materials. The FP provides a much higher surface area for weathering whereas in actual products only a thin surface layer may undergo some aging reactions. During this aging process, further release of ENM from the matrix fragments can occur as shown for TiO_2 release from paint fragments.[27]

Example case study: Nanoparticulate organic pigment in polypropylene

One of the SUN case studies is a nanoscale, transparent, solid organic pigment incorporated into a polymer matrix of polypropylene (case study 3, Table 1). Figure 1 shows different life cycle stages of both the nano-pigment and the nano-free reference matrix that are simulated within SUN. The organic pigment nanoparticles were mixed with the plastic and processed by hot melt extrusion and granulation. The resulting granulates had cylindrical shapes with a length of approximately 4 mm and a diameter about 2 mm. Representative for a final product such as car bumpers, sheets of the nano-composite were produced by melt pressing of the granulates. To obtain FP, cryomilling of the compounded granulates was performed. For this, granulates were frozen to cryogenic temperatures (at -193°C, liquid N_2) to maximize their brittleness. In the mill (impeller breaker, Pallmann PPL 18), the impeller rotated at 10,000 rpm (92 m/s circumferential speed). Within 40 minutes, the total amount of 1 kg of the granulates passed through the 0.3 mm gap between the rotor/stator impeller.

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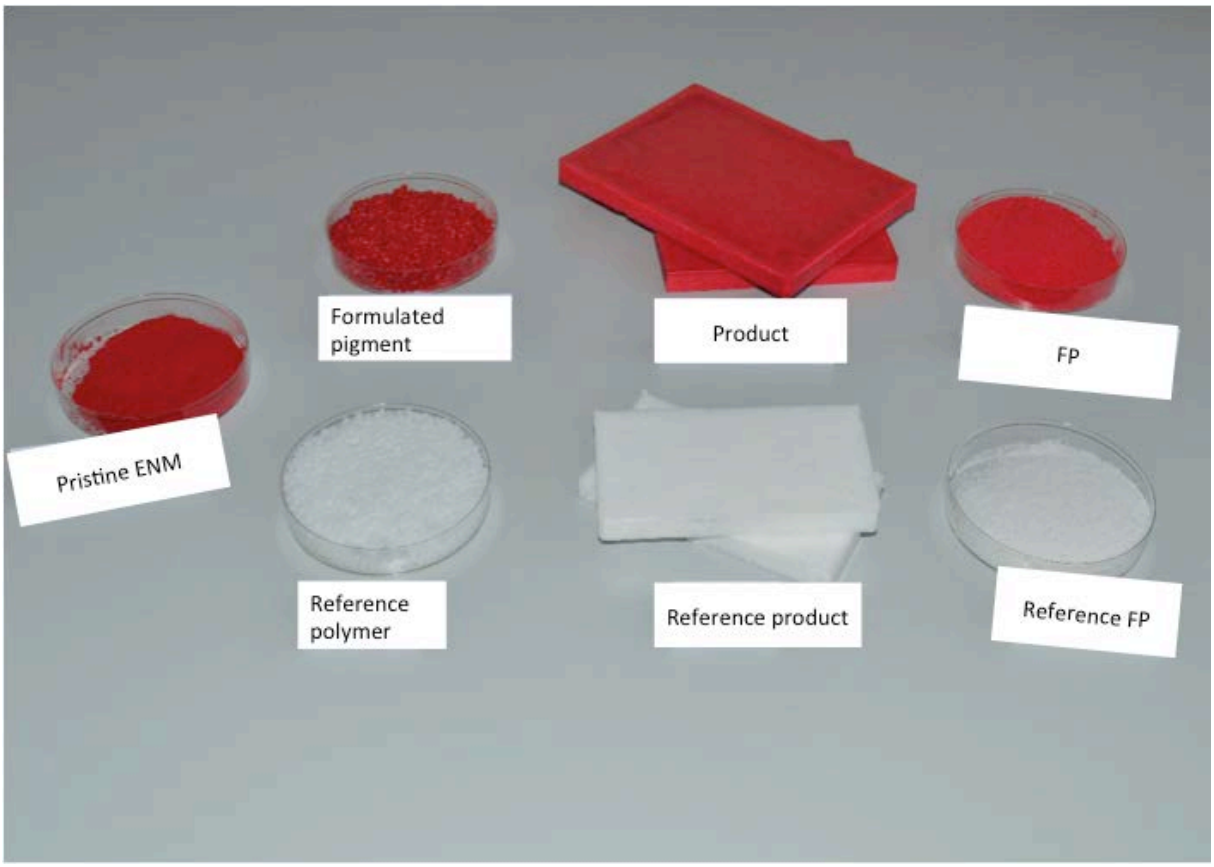
239 Granulates, sheets and FP were produced for the pure PP plastic as well which serve as a
240 reference during fate testing.
241



242
243 *Figure 1. The SUN nanoparticulate solid organic pigment in polymer case study (red, top)*
244 *with pure polymer reference (white, bottom): pristine ENM (on left), formulated product*
245 *after compounding, final nano-composite sheets and fragmented product (FP).*
246
247 To determine the size distributions of the FP, the material was suspended in water
248 containing SDS (sodiumdodecylsulfate) at 0.5 g/l and the sample was probe sonicated. The
249 samples were prepared at a concentration of 1 g/l. The apparatus used for laser diffraction
250 analysis was a Mastersizer 3000 (Malvern). The resulting mass-based size distributions
251 (Figure 2) show clearly that the vast majority of fragments resulting from cryomilling is far
252 from inhalable sizes[43]. Therefore, the FP produced by cryomilling will be used within SUN for
253 ecotoxicological testing, but is not useful for inhalation studies.
254 To achieve a separation of the smallest possible fragments, dry sieving was performed with a
255 mesh size of 100 µm (sieve 14046173 by Retsch). The size distributions of the SFP were

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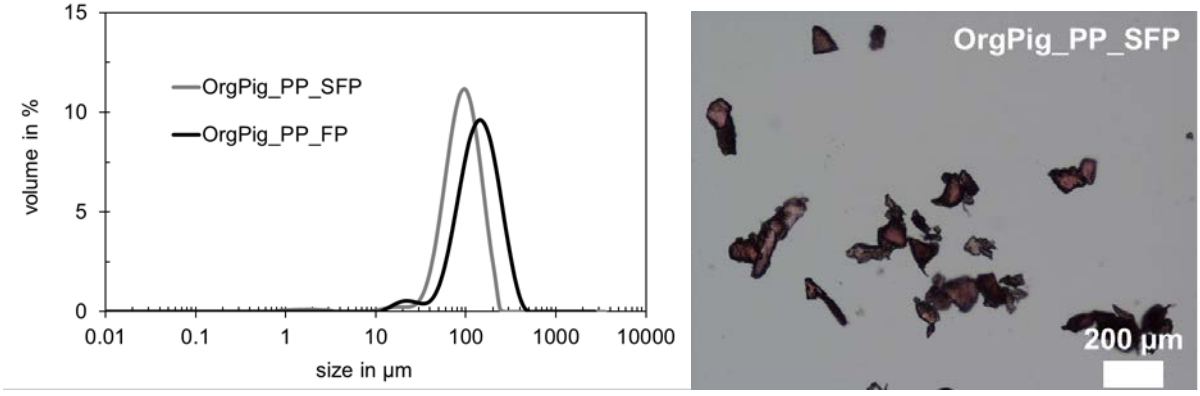
obtained in the liquid by laser diffraction as described above (Figure 2). Obviously, the size distributions of the SFP shifted towards smaller particle sizes with maximum sizes in the range of 200 µm. The hydrophobic character of the PP matrix presumably lead to a shift of the size distribution towards larger fragments due to agglomeration of the fragments in the dispersion. However, the result from laser diffraction is valuable as it clearly demonstrates that sieving successfully eliminated the coarse fraction of the FP. Additionally, images from optical microscopy were taken (Figure 2) which visually confirmed the elimination of the coarse fraction of the FP. In addition, Figure 2 demonstrates that the behavior during cryomilling is dominated by the matrix. No obvious influence from the nano-filler on the resulting size distributions can be observed.

On the determined mass-based scale, the amounts of the SFP were only 0.3-0.5% of the FP resulting from cryomilling respectively. With this, the fraction of the smallest possible fragments - which is, however, not in the inhalable size range – can be considered very low on a mass-based scale but may represent a high particle number. Nevertheless, the SFP will also be provided for ecotoxicological fate testing within SUN.

Studies within SUN about mechanical processing by sanding have already proven to deliver a higher content of smaller sizes compared to cryomilling (data will be published separately). These smaller sizes are detectable especially in the aerosol on a number-based metric, not so easily on the entire collected dust in volume or mass metrics. Therefore it is planned within SUN to use sanding dust for toxicological testing as well.



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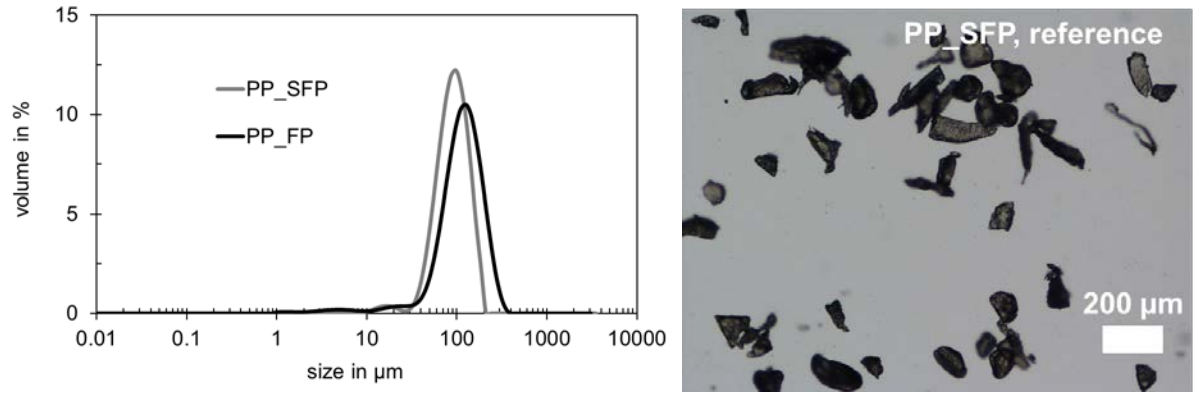

Figure 2. Size distributions of the fragmented product (FP) (black line) and the sieved fragmented products (SFP) (grey line) determined by laser diffraction; on the right a microscope image of the SFP is shown; the PP with organic pigment is shown on top, the control without pigment on bottom.

Conclusions and Outlook

The focus on aging and release of nanomaterials from products is relevant because of the importance to holistically address the life cycle of nanoproducts. The form of ENM that reaches the environment, or that consumers are exposed to, often depends on the nature of the matrix in which the ENM were incorporated. Thus, it is necessary to investigate the effects and fate of these released materials and compare them to pristine nanomaterials for which a huge amount of data is already available. These investigations will need to elucidate whether pristine and aged/released ENM have similar or different behavior and effects. The progress in this field is currently hampered by methodological difficulties in how to obtain released/aged materials in quantities sufficiently high for further testing. In this perspective, besides characterizing and quantifying nanomaterials released from products exposed to various environmental stressors we here show how to obtain a material fraction that is comparable to the materials that were reported to be released under real-world conditions[13] and how to isolate nanomaterials in amounts needed for further testing.

We acknowledge that the FP and WFP obtained by our approach are not the materials released from products, but they represent an approximation and allow the production of hundred gram quantities of materials for testing (see Table 1). It may be necessary to use

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more than one process to obtain FP or especially WFP for each matrix as the same material may be exposed to different stresses during the life cycle of the products.

A further size fractionation can be performed to isolate a SFP fraction that is more representative for inhalation studies (PM10, PM2.5 for instance), however, only minute amounts in terms of mass of the fragments obtained by our approach are actually small enough for such studies. This finest fraction is clearly the most relevant for human toxicology studies but also for ecotoxicological studies this fine fraction might be of interest.

The approach presented in this perspective is centered on the use phase of nano-products and can equally be applied to the end-of-life stage. This is particularly important as significant release could occur in the end-of-life stage (e.g. shredding, incineration, landfilling, recycling), especially for products where the ENM are bound in a matrix[11, 12].

Acknowledgements

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References

1. Stark, W. J.; Stoessel, P. R.; Wohlleben, W.; Hafner, A., Industrial applications of nanoparticles. *Chemical Society Reviews* **2015,** *44*, 5793-5805.
2. Nanodatabase The Nanodatabase http://nanodb.dk/. DTU Environment, Danish Consumer Council and theDanish Ecological Council.
3. Kingston, C.; Zepp, R.; Andrady, A.; Boverhof, D.; Fehir, R.; Hawkins, D.; Roberts, J.; Sayre, P.; Shelton, B.; Sultan, Y.; Vejins, V.; Wohlleben, W., Release characteristics of selected carbon nanotube polymer composites. *Carbon* **2014,** *68*, 33-57.
4. Benedix, R.; Dehn, F.; Quaas, J.; Orgass, M., Application of titanium dioxide photocatalysis to create self-cleaning building materials. *Lacer* **2000,** *5*, 157-168.
5. Ruot, B.; Plassais, A.; Olive, F.; Guillot, L.; Bonafous, L., TiO2-containing cement pastes and mortars: Measurements of the photocatalytic efficiency using a rhodamine B-based colourimetric test. *Sol. Energy* **2009,** *83*, 1794-1801.
6. Nohynek, G. J.; Lademann, J.; Ribaud, C.; Roberts, M. S., Grey goo on the skin? Nanotechnology, cosmetic and sunscreen safety. *Critical Reviews in Toxicology* **2007,** *37*, 251-277.

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7. Khanna, A. S., Nanotechnology in High Performance Paint Coatings. *Asian J. Exp. Sci.* **2008,** *21*, 25-32.
8. Peters, R.; ten Dam, G.; Bouwmeester, H.; Helsper, H.; Allmaier, G.; von der Kammer, F.; Ramsch, R.; Solans, C.; Tomaniova, M.; Hajslova, J.; Weigel, S., Identification and characterization of organic nanoparticles in food. *Trac-Trends in Analytical Chemistry* **2011,** *30*, 100-112.
9. Som, C.; Berges, M.; Chaudhry, Q.; Dusinska, M.; Fernandes, T. F.; Olsen, S. I.; Nowack, B., The Importance of Life Cycle Concepts for the Development of Safe Nanoproducts. *Toxicol.* **2010,** *269*, 160–169.
10. Boldrin, A.; Hansen, S. F.; Baun, A.; Hartmann, N. I. B.; Astrup, T. F., Environmental exposure assessment framework for nanoparticles in solid waste. *Journal of Nanoparticle Research* **2014,** *16*, 2394.
11. Nowack, B.; David, R. M.; Fissan, H.; Morris, H.; Shatkin, J. A.; Stintz, M.; Zepp, R.; Brouwer, D., Potential release scenarios for carbon nanotubes used in composites. *Environment International* **2013,** *59*, 1-11.
12. Walser, T.; Gottschalk, F., Stochastic fate analysis of engineered nanoparticles in incineration plants. *Journal of Cleaner Production* **2014,** *80*, 241-251.
13. Froggett, S. J.; Clancy, S. F.; Boverhof, D. R.; Canady, R. A., A review and perspective of existing research on the release of nanomaterials from solid nanocomposites. *Particle and Fibre Toxicology* **2014,** *11*, 17.
14. Duncan, T. V.; Pillai, K., Release of Engineered Nanomaterials from Polymer Nanocomposites: Diffusion, Dissolution, and Desorption. *ACS Applied Materials & Interfaces* **2015,** *7*, 2-19.
15. Al-Kattan, A.; Wichser, A.; Vonbank, R.; Brunner, S.; Ulrich, A.; Zuin, S.; Arroyo, Y.; Golanski, L.; Nowack, B., Characterization of materials released into water from paint containing nano-SiO2. *Chemosphere* **2015,** *119*, 1314–1321.
16. Al-Kattan, A.; Wichser, A.; Vonbank, R.; Brunner, S.; Ulrich, A.; Zuin, S.; Nowack, B., Release of TiO_2 from paints containing pigment-TiO_2 or nano-TiO_2 by weathering. *Environmental Science: Processes & Impacts* **2013,** *15*, 2186–2193.
17. Zuin, S.; Gaiani, M.; Ferrari, A.; Golanski, L., Leaching of nanoparticles from experimental water-borne paints under laboratory test conditions. *J Nanopart Res* **2014,** *16*, 2185.
18. Cena, L. G.; Peters, T. M., Characterization and Control of Airborne Particles Emitted During Production of Epoxy/Carbon Nanotube Nanocomposites. *Journal of Occupational and Environmental Hygiene* **2011,** *8*, 86-92.
19. Wohlleben, W.; Meier, M. W.; Vogel, S.; Landsiedel, R.; Cox, G.; Hirth, S.; Tomovic, Z., Elastic CNT-polyurethane nanocomposite: synthesis, performance and assessment of fragments released during use. *Nanoscale* **2013,** *5*, 369-380.
20. Wohlleben, W.; Vilar, G.; Fernández-Rosas, E.; González-Gálvez, D.; Gabriel, C.; Hirth, S.; Frechen, T.; Stanley, D.; Gorham, J.; Sung, L.-P.; Hsueh, H.-C.; Chuang, Y.-F.; Nguyen, T.; Vazquez-Campos, S., A pilot interlaboratory comparison of protocols that simulate aging of nanocomposites and detect released fragments. *Environmental Chemistry* **2014,** *11*, 402-418.
21. Auffan, M.; Pedeutour, M.; Rose, J.; Masion, A.; Ziarelli, F.; Borschneck, D.; Chaneac, C.; Botta, C.; Chaurand, P.; Labille, J.; Bottero, J. Y., Structural Degradation at the Surface of a

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TiO_2-Based Nanomaterial Used in Cosmetics. *Environmental Science & Technology* **2010,** *44*, 2689-2694.

22. Botta, C.; Labille, J.; Auffan, M.; Borschneck, D.; Miche, H.; Cabie, M.; Mason, A.; Rose, J.; Bottero, J. Y., TiO_2-based nanoparticles released in water from commercialized sunscreens in a life-cycle perspective: Structures and quantities. *Environmental Pollution* **2011,** *159*, 1543-1548.

23. Labille, J.; Feng, J. H.; Botta, C.; Borschneck, D.; Sammut, M.; Cabie, M.; Auffan, M.; Rose, J.; Bottero, J. Y., Aging of TiO_2 nanocomposites used in sunscreen. Dispersion and fate of the degradation products in aqueous environment. *Environmental Pollution* **2010,** *158*, 3482-3489.

24. Bigorgne, E.; Foucaud, L.; Lapied, E.; Labile, J.; Botta, C.; Sirguey, C.; Falla, J.; Rose, J.; Joner, E. J.; Rodius, F.; Nahmani, J., Ecotoxicological assessment of TiO(2) byproducts on the earthworm Eisenia fetida. *Environmental Pollution* **2011,** *159*, 2698-2705.

25. Foltete, A. S.; Masfaraud, J. F.; Bigorgne, E.; Nahmani, J.; Chaurand, P.; Botta, C.; Labille, J.; Rose, J.; Ferard, J. F.; Cotelle, S., Environmental impact of sunscreen nanomaterials: Ecotoxicity and genotoxicity of altered TiO2 nanocomposites on Vicia faba. *Environmental Pollution* **2011,** *159*, 2515-2522.

26. Fouqueray, M.; Dufils, B.; Vollat, B.; Chaurand, P.; Botta, C.; Abacci, K.; Labille, J.; Rose, J.; Garric, J., Effects of aged TiO2 nanomaterial from sunscreen on Daphnia magna exposed by dietary route. *Environmental Pollution* **2012,** *163*, 55-61.

27. Al-Kattan, A.; Wichser, A.; Zuin, S.; Arroyo, Y.; Golanski, L.; Ulrich, A.; Nowack, B., Behavior of TiO2 released from nano-TiO2-containing paint and comparison to pristine nano-TiO2. *Environmental Science & Technology* **2014,** *48*, 6710−6718.

28. Mitrano, D. M.; Motellier, S.; Clavaguera, S.; Nowack, B., Review of nanomaterial aging and transformations through the life cycle of nano-enhanced products. *Environment International* **2015,** *77*, 132-147.

29. Nowack, B.; Ranville, J. F.; Diamond, S.; Gallego-Urrea, J. A.; Metcalfe, C.; Rose, J.; Horne, N.; Koelmans, A. A.; Klaine, S. J., Potential scenarios for nanomaterial release and subsequent alteration in the environment. *Environ. Toxicol. Chem.* **2012,** *31*, 50-59.

30. Levard, C.; Reinsch, B. C.; Michel, F. M.; Oumahi, C.; Lowry, G. V.; Brown, G. E., Sulfidation Processes of PVP-Coated Silver Nanoparticles in Aqueous Solution: Impact on Dissolution Rate. *Environmental Science & Technology* **2011,** *45*, 5260-5266.

31. Lorenz, C.; Windler, L.; Lehmann, R. P.; Schuppler, M.; Von Goetz, N.; Hungerbühler, K.; Heuberger, M.; Nowack, B., Characterization of silver release from commercially available functional (nano)textiles. *Chemosphere* **2012,** *89*, 817–824.

32. Windler, L.; Lorenz, C.; Von Goetz, N.; Hungerbuhler, H.; Amberg, M.; Heuberger, M.; Nowack, B., Release of titanium dioxide from textiles during washing. *Environ Sci Technol* **2012,** *46*, 8181−8188.

33. ASTM, ASTM G195 - 13a. Standard Guide for Conducting Wear Tests Using a Rotary Platform Abraser. In 2013.

34. Schlagenhauf, L.; Buerki-Thurnherr, T.; Kuo, Y.-Y.; Wichser, A.; Nüesch, F.; Wick, P.; Wang, J., Carbon Nanotubes Released from an Epoxy-Based Nanocomposite: Quantification and Particle Toxicity. *Environmental Science & Technology* **2015**.

35. Zuin, S.; Massari, A.; Ferrari, A.; Golanski, L., Formulation effects on the release of silica dioxide nanoparticles from paint debris to water. *Science of the Total Environment* **2014,** *476*, 298-307.

This is a post-prinnt version of Nowack et al. (2016). Meeting the Needs for Released Nanomaterials Required for Further Testing—The SUN Approach. Environmental Science and Technology, 50(6), 2747-2753.
The printed version of the paper is availbale at: DOI: 10.1021/acs.est.5b04472

36. Kaegi, R.; Ulrich, A.; Sinnet, B.; Vonbank, R.; Wichser, A.; Zuleeg, S.; Simmler, H.; Brunner, S.; Vonmont, H.; Burkhardt, M.; Boller, M., Synthetic TiO_2 nanoparticle emission from exterior facades into the aquatic environment. *Environ. Pollut.* **2008,** *156*, 233-239.
37. Kaegi, R.; Sinnet, B.; Zuleeg, S.; Hagendorfer, H.; Mueller, E.; Vonbank, R.; Boller, M.; Burkhardt, M., Release of silver nanoparticles from outdoor facades. *Environmental Pollution* **2010,** *158*, 2900-2905.
38. Kaiser, J.-P.; Roesslein, M.; Diener, L.; Wick, P., Human Health Risk of Ingested Nanoparticles That Are Added as Multifunctional Agents to Paints: an In Vitro Study. *PLoS ONE* **2013,** *8*, e83215.
39. Smulders, S.; Luyts, K.; Brabants, G.; Landuyt, K. V.; Kirschhock, C.; Smolders, E.; Golanski, L.; Vanoirbeek, J.; Hoet, P. H., Toxicity of Nanoparticles Embedded in Paints Compared with Pristine Nanoparticles in Mice. *Toxicological Sciences* **2014,** *141*, 132-140.
40. Saber, A. T.; Koponen, I. K.; Jensen, K. A.; Jacobsen, N. R.; Mikkelsen, L.; Moller, P.; Loft, S.; Vogel, U.; Wallin, H., Inflammatory and genotoxic effects of sanding dust generated from nanoparticle-containing paints and lacquers. *Nanotoxicology* **2012,** *6*, 776-788.
41. Le Bihan, O.; Shandilya, N.; Gheerardyn, L.; Guillon, O.; Dore, E.; Morgeneyer, M., Investigation of the Release of Particles from a Nanocoated Product. *Advances in Nanoparticles* **2013,** *2*, 39-44.
42. ISO, ISO 4892-1: Plastics - Methods of exposure to laboratory light sources - Part 1: General guidance. ISO 4892-2: Plastics - Methods of exposure to laboratory light sources - Part 2: Xenon-arc sources.
43. Heyder, J., Deposition of Inhaled Particles in the Human Respiratory Tract and Consequences for Regional Targeting in Respiratory Drug Delivery. *Proceedings of the American Thoracic Society* **2004,** *1*, 315-320.